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(54) CURABLE COMPOSITION FOR MOLDING AND MOLDED ITEM OBTAINED BY  
CURING SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a curable composition for molding which is excellent in processibility and curability by compounding an alkenylated vinyl polymer and a hydrosilylated compound as the essential ingredients.

SOLUTION: A vinyl polymer having at least one alkenyl group represented by  $\text{CH}_2=\text{C}(\text{R}_1)-$  (wherein  $\text{R}_1$  is H or methyl) is used. A vinyl polymer formed by using at least 40 wt.% (meth) acrylic acid-based monomer is especially preferable. The mol.wt. distribution is preferably lower than 1.8. The vinyl polymer is preferably one formed by living free-radical polymerization, especially atom transfer free-radical polymerization. A compound such as a linear polysiloxane or a cyclic siloxane can be used as the hydrosilylated compound. The vinyl polymer and the hydrosilylated compound are compounded in a molar ratio of alkenyl group to hydrosilyl group of 5-0.2.

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## CLAIMS

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[Claim(s)]

[Claim 1] The vinyl system polymer,  $\text{CH}_2=\text{C}(\text{R}_1)$ - which have at least one alkenyl radical expressed with the following 2 component:(A) general formulas (1) (1)

(R<sub>1</sub> shows hydrogen or a methyl group among a formula.)

(B) The hardenability constituent for shaping which uses a hydrosilyl radical content compound as an indispensable component.

[Claim 2] (A) The hardenability constituent for shaping according to claim 1 whose molecular weight distribution of the vinyl system polymer of a component are less than 1.8.

[Claim 3] (A) The hardenability constituent for shaping given in claim 1 whose vinyl system polymer of a component is an acrylic (meta) polymer, or any 1 term of 2.

[Claim 4] (A) The hardenability constituent for shaping given in any 1 term of claims 1-3 whose vinyl system polymers of a component are acrylic polymers.

[Claim 5] (A) The hardenability constituent for shaping given in any 1 term of claims 1-4 characterized by manufacturing the vinyl system polymer of a component by the living radical polymerization method.

[Claim 6] (A) The hardenability constituent for shaping given in any 1 term of claims 1-5 characterized by manufacturing the vinyl system polymer of a component by the atomic migration radical polymerization method.

[Claim 7] (A) The hardenability constituent for shaping given in any 1 term of claims 1-6 whose components are the vinyl system polymers which have the alkenyl radical shown in a general formula (1) at at least one chain end.

[Claim 8] (A) The process of the following [ component ] : by carrying out the polymerization of the (1) vinyl system monomer by the atomic migration radical polymerization method, manufacture the vinyl system polymer which has the end structure shown by the general formula (2), and it is  $-\text{C}(\text{R}_2)(\text{R}_3)(\text{X})$ . (2)

R<sub>2</sub> and R<sub>3</sub> show among a formula the radical combined with the ethylene nature partial saturation radical of a vinyl system monomer. X shows chlorine, a bromine, or iodine.

(2) The hardenability constituent for shaping given in any 1 term of claims 1-7 which are the vinyl system polymers obtained by; which changes the end halogen of said polymer into the substituent which has the alkenyl radical of a general formula (1).

[Claim 9] (A) The process of the following [ component ] : the hardenability constituent for shaping given in any 1 term of claims 1-7 which manufacture a vinyl system polymer and (2) Are the vinyl system polymers obtained by; to which the compound which continues and has at least two low alkenyl radicals of polymerization nature is made to react by carrying out the polymerization of the (1) vinyl system monomer by the living radical polymerization method.

[Claim 10] The Plastic solid which makes any 1 term come to harden the hardenability constituent for shaping of a publication among claims 1-9.

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[Translation done.]

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the Plastic solid which makes it come to harden the hardenability constituent for shaping, and this. In more detail, an alkenyl radical content vinyl system polymer and a hydrosilyl radical content compound are used as an indispensable component, and it is related with the Plastic solid which makes it come to harden the hardenability constituent for shaping and this constituent which obtain a hardened material with shaping.

[0002]

[Description of the Prior Art] The Plastic solid which uses a vinyl system polymer and an acrylic (meta) polymer as a principal component is acquired by \*\*\*\*(ing) the polymer of the amount of macromolecules in the state of heating, and fabricating it using a roll, a mill, etc., with various additives. When fabricating thermoplastics or thermosetting resin, it is necessary to fabricate in the heating melting condition, and there is a problem of being unable to use a weak additive for heat. Moreover, although it is obtained by carrying out vulcanization shaping after kneading compounding agents, such as a filler and a vulcanizing agent, to an unvulcanized rubber when fabricating the rubber represented by acrylic rubber in this case, it is hard to become smooth [ at the time of sheeting ] in adhering to a roll at the time of kneading in addition to the above-mentioned trouble, or is a non-fluidity at the time of shaping -- etc. -- the badness of workability, the lateness of a vulcanization rate, or the postcure of long duration is required -- etc. -- there is a problem also in the badness of hardenability.

[0003]

[Problem(s) to be Solved by the Invention] This invention aims at offering the Plastic solid which has the hardenability constituent for shaping which was excellent in workability and was excellent in hardenability and sufficient mechanical characteristic which makes it come to harden this, thermal resistance, and oilproof by using the liquefied polymer which can knead compounding agents, such as a filler.

[0004]

[Means for Solving the Problem] This invention is vinyl system polymer and  $\text{CH}_2=\text{C}(\text{R}1)-$  which has at least one alkenyl radical expressed with the following 2 component:(A) general formulas (1). (1) (R1 shows hydrogen or a methyl group among a formula.) (B) It is the Plastic solid which makes it come to harden the hardenability constituent for shaping and this which use a hydrosilyl radical content compound as an indispensable component.

[0005]

[Embodiment of the Invention] This invention is vinyl system polymer and  $\text{CH}_2=\text{C}(\text{R}1)-$  which has at least one alkenyl radical expressed with the following 2 component:(A) general formulas (1). (1) (R1 shows hydrogen or a methyl group among a formula.) (B) It is the Plastic solid which makes it come to harden the hardenability constituent for shaping and this

which use a hydrosilyl radical content compound as an indispensable component.

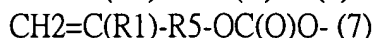
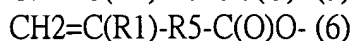
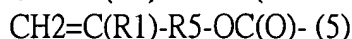
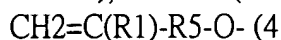
[0006] Below, the hardenability constituent for shaping of this invention is explained in full detail.

As an alkenyl radical expressed with the above-mentioned general formula (1) which is the cross-linking radical of the vinyl system polymer of [vinyl system (A) Polymer (A) of component] component The alkenyl radical of the hydrocarbon system expressed with the following general formula (3); The alkenyl radical which has the ether linkage expressed with a general formula (4), Alkenyl radical; combined with a principal chain through an oxygen atom, such as an alkenyl radical which has carbonate association expressed with the alkenyl radical and general formula (7) which have the ester bond expressed with a general formula (5) and (6), is mentioned.



(R1 is the same as that of what was mentioned above among a formula.) R4 shows the divalent hydrocarbon group of direct coupling or carbon numbers 1-20.

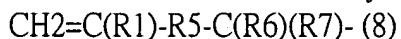
In the above-mentioned general formula (3), although not limited especially as R4,  $-(\text{CH}_2)_n-$  (n is the integer of 0-10),  $-\text{CH}_2\text{CH}(\text{CH}_3)-$ ,  $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2-$ , etc. are mentioned, for example.



(R1 is the same as that of what was mentioned above among a formula.) R5 shows the divalent organic radical of the carbon numbers 1-20 which may contain direct coupling or one or more ether linkage.

In the above-mentioned general formula (4), (5), (6), and (7), although not limited especially as R5  $-(\text{CH}_2)_n-$  and (n For example, integer) of 0-20,  $-\text{CH}_2\text{CH}(\text{CH}_3)-$ ,  $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2-$ ,  $-\text{CH}_2\text{OCH}_2\text{CH}_2-$ ,  $-\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2-$ ; o-, m-, p-C<sub>6</sub>H<sub>4</sub>-, o-, m-, p-CH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-, o-, m-, and p-CH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>- etc. is mentioned.

[0007] Moreover, the radical which has the electron withdrawing group expressed with a general formula (8) is also mentioned as an alkenyl radical of a general formula (1).



(R1 and R5 are the same as that of what was mentioned above among a formula.) Another side shows [ the electron withdrawing group to which both R6 and R7 stabilize carbanion C-, or one side ] the alkyl group or phenyl group of hydrogen or carbon numbers 1-10 by the above-mentioned electron withdrawing group.

Although not limited especially as an electron withdrawing group of R6 and R7 in the above-mentioned general formula (8),  $-\text{CO}_2\text{R}$  (ester group) and  $-\text{C}(\text{O})\text{R}$  (keto radical),  $-\text{CON}(\text{R}_2)$  (amide group),  $-\text{COSR}$  (thioester radical),  $-\text{CN}$  (nitrile group),  $-\text{NO}_2$  (nitro group), etc. are mentioned, for example. Substituent R shows the alkyl group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, or the aralkyl radical of carbon numbers 7-20, and its alkyl group or phenyl group of carbon numbers 1-10 is desirable. Especially as R6 and R7,  $-\text{CO}_2\text{R}$  and  $-\text{C}(\text{O})\text{R}$  and  $-\text{CN}$  are desirable.

[0008] (A) It is not limited especially as a monomer which forms the principal chain of the vinyl system polymer of a component, but various kinds of things can be used. If it illustrates, an acrylic acid (meta), a methyl acrylate (meta), An ethyl acrylate, acrylic-acid (meta)-n-propyl, acrylic-acid (meta) isopropyl, (Meta) Acrylic-acid-n-butyl, isobutyl acrylate (meta), (Meta) Acrylic-acid-tert-butyl, acrylic-acid (meta)-n-pentyl, (Meta) Acrylic-acid-n-hexyl, acrylic-acid (meta) cyclohexyl, (Meta) Acrylic-acid-n-heptyl, acrylic-acid (meta)-n-octyl, (Meta) 2-ethylhexyl acrylate, acrylic-acid (meta) nonyl, (Meta) Acrylic-acid DESHIRU, acrylic-acid (meta) dodecyl, acrylic-acid (meta) phenyl, (Meta) Acrylic-acid toluy, acrylic-acid (meta) benzyl, acrylic-acid (meta)-2-methoxy ethyl, (Meta) Acrylic-acid-3-methoxy butyl, acrylic-acid (meta)-2-hydroxyethyl, (Meta) 2-hydroxypropyl acrylate, acrylic-acid (meta) stearyl, (Meta) Metaglycidyl acrylate, acrylic-acid (meta)-2-aminoethyl, (Meta) gamma-(methacryloyl oxypropyl) trimethoxysilane, the ethyleneoxide addition product of an acrylic acid (meta), Acrylic-acid trifluoromethyl methyl, an acrylic-acid

(meta)-2-trifluoro methylethyl, (Meta) Acrylic-acid-2-perfluoro ethyl ethyl, acrylic-acid (meta)-2-perfluoro ethyl-2-perfluoro butyl ethyl, (Meta) Acrylic-acid-2-perfluoro ethyl, acrylic-acid (meta) perfluoro methyl, (Meta) Acrylic-acid JIPA fluoro methyl methyl, acrylic-acid (meta) 2-perfluoro methyl-2-perfluoro ethyl methyl, (Meta) Acrylic-acid-2-perfluoro hexyl ethyl, acrylic-acid (meta)-2-perfluoro DESHIRU ethyl, (Meta) Acrylic-acid (meta) system monomers, such as acrylic-acid-2-perfluoro hexadecyl ethyl; Styrene, (Meta) Styrene system monomers, such as vinyltoluene, alpha methyl styrene, KURORU styrene, a styrene sulfonic acid, and its salt; Perfluoro ethylene, Fluorine content vinyl monomers, such as a perfluoro propylene and vinylidene fluoride; Vinyltrimetoxysilane, Silicon content vinyl system monomers, such as vinyltriethoxysilane; A maleic anhydride, Monoalkyl ester and dialkyl ester of a maleic acid and a maleic acid; A fumaric acid, Monoalkyl ester and dialkyl ester of a fumaric acid; Maleimide, Methyl maleimide, ethylmaleimide, propyl maleimide, butylmaleimide, Hexyl maleimide, octyl maleimide, dodecyl maleimide, stearyl maleimide, Maleimide system monomers, such as phenyl maleimide and cyclohexyl maleimide; Acrylonitrile, Nitrile group content vinyl system monomers, such as a methacrylonitrile; Acrylamide, Amide group content vinyl system monomers, such as methacrylamide; Vinyl acetate, Conjugated dienes, such as alkenes; butadienes, such as vinyl ester; ethylene, such as propionic-acid vinyl, vinyl pivalate, benzoic-acid vinyl, and cinnamic acid vinyl, and a propylene, and an isoprene; a vinyl chloride, a vinylidene chloride, an allyl chloride, allyl alcohol, etc. are mentioned. These may be used independently, and even if they use two or more sorts together, they are not cared about. In addition, an acrylic acid (meta) shows an acrylic acid and/or a methacrylic acid according to the above-mentioned transcription.

[0009] The acrylic (meta) polymer obtained by compounding in the above-mentioned monomer, using an acrylic-acid (meta) system monomer 40% of the weight or more in the vinyl system polymer which has at least one alkenyl radical shown in a general formula (1) is more desirable from a physical-properties side. Moreover, the acrylic polymer obtained by compounding in the above-mentioned monomer, using an acrylic-acid system monomer 40% of the weight or more in the vinyl system polymer which has at least one alkenyl radical shown in a general formula (1) is still more desirable from a physical-properties side.

[0010] It is not limited about especially the molecular weight distribution of the vinyl system polymer which has at least one alkenyl radical, i.e., the ratio of weight average molecular weight (Mw) and number average molecular weight (Mn), (Mw/Mn). however, the viscosity at the time of considering as a hardenability constituent -- low -- stopping -- handling -- easy -- carrying out -- in addition -- and in order to acquire sufficient hardened material physical properties, narrow one of molecular weight distribution is desirable. It is 1.3 or less still more preferably 1.4 or less still more preferably 1.5 or less still more preferably 1.6 or less still more preferably 1.7 or less more preferably [ as a value of molecular weight distribution, less than 1.8 are desirable, and ]. As for measurement of molecular weight distribution, measuring with gel permeation chromatography (GPC) is most common. Chloroform and THF can be used as a mobile phase, a polystyrene gel column can be used as a column, and number average molecular weight etc. can be calculated by polystyrene conversion.

[0011] Although not limited especially about the molecular weight of the vinyl system polymer which has at least one alkenyl radical, it is desirable that it is in the range of 500-100000. The original property of a vinyl system polymer is it hard to be discovered that molecular weight is 500 or less, and handling becomes it difficult that it is 100000 or more.

[0012] The vinyl system polymer which has at least one alkenyl radical can be obtained by various polymerization methods, and especially the approach is not limited. However, the method of introducing a direct alkenyl radical by the radical polymerization method from the point of the versatility of a monomer and the ease of control, or obtaining the vinyl system polymer which has a specific functional group convertible into an alkenyl radical at one step or several steps of reactions, and obtaining the vinyl system polymer which has at least one alkenyl radical by changing this specific functional group into an alkenyl radical is more desirable.

[0013] The radical polymerization method used in the approach of compounding the vinyl system polymer which has a specific functional group containing an alkenyl radical can classify into the "control radical polymerization method" which can introduce a specific functional group into "the general radical polymerization method" to which copolymerization of the monomer which has a specific functional group, and the vinyl system monomer is only carried out, and the location controlled [ end ], using an azo system compound, a peroxide, etc. as a polymerization initiator.

[0014] Although "a general radical polymerization method" is a simple approach, since the monomer which has a specific functional group by this approach is not introduced into a probable polymer, when it is going to obtain a polymer with the high rate of organic-functions-izing, it is necessary to use this monomer quite in large quantities, and there is a trouble that the rate of a polymer that this specific functional group is not introduced becomes large, by little use conversely. Moreover, since it is a free radical polymerization, the trouble that only a large polymer with high viscosity is obtained also has molecular weight distribution.

[0015] A "control radical polymerization method" can be classified into the "living radical polymerization method" the polymer of the molecular weight as a design is obtained mostly, by growing without the "chain transfer agent method" the vinyl system polymer which has a functional group at the end is obtained, and a polymerization growth end causing termination reaction etc. by performing a polymerization using the chain transfer agent which has a further specific functional group.

[0016] Although a "chain transfer agent method" can obtain a polymer with the high rate of organic-functions-izing, the chain transfer agent which has quite a lot of specific functional groups to an initiator is required for it, and it has a problem on the financial side also including processing. Moreover, like the above-mentioned "general radical polymerization method", since it is a free radical polymerization, the trouble that it is large and only a polymer with high viscosity is obtained also has molecular weight distribution.

[0017] While termination reaction cannot occur easily and the narrow ( $M_w/M_n$  is 1.1 to about 1.5) polymer of molecular weight distribution is obtained though it is the radical polymerization by which control is made difficult since the termination reaction a "living radical polymerization method" has a high rate of polymerization, and according to coupling of radicals etc. tends to occur unlike these polymerization methods, molecular weight is freely controllable with the preparation ratio of a monomer and an initiator.

[0018] Therefore, a "living radical polymerization method" has narrow molecular weight distribution, and is more desirable as the manufacture approach of a vinyl system polymer of having the above-mentioned specific functional group for the monomer which can obtain a polymer with low viscosity upwards and has a specific functional group since [ of a polymer ] it can introduce into the location of arbitration mostly.

[0019] In addition, although living polymerization means the polymerization to which an end always continues having activity and the chain grows in the narrow sense, the pseudo-living polymerization which grows while that by which the end was inactivated, and the activated thing are generally in an equilibrium state is also contained. The definition in this invention is also the latter.

[0020] As for the "living radical polymerization method", research is positively made into groups various in recent years. As the example, for example A journal OBU American chemical society (J. Am.Chem.Soc.), 1994, 116 volumes, the thing using a cobalt porphyrin complex as shown in 7943 pages, Macro leakage-at-bulb KYURUZU (Macromolecules), 1994, The thing using radical scavengers, such as 27 volumes and a nitroxide compound as shown in 7228 pages, "The atomic migration radical polymerization" (Atom Transfer Radical Polymerization:ATRP) etc. which makes an organic halogenide etc. an initiator and makes a transition metal complex a catalyst is raised.

[0021] Also in a "living radical polymerization method", an organic halogenide or a halogenation sulfonyl compound An initiator, "The atomic migration radical polymerization method" which carries out the polymerization of the vinyl system monomer by making a transition metal complex into a catalyst As the manufacture approach of a vinyl system polymer of in addition to the description of the above-mentioned "living radical polymerization method" having a halogen comparatively advantageous to a functional-group



conversion reaction etc. at the end, and having a specific functional group from the degree of freedom of a design of an initiator or a catalyst being large, it is still more desirable. As this atomic migration radical polymerization method, Matyjaszewski et al. [ for example, ], Journal OBU American chemical society (J. Am.Chem.Soc.) 1995, 117 volumes, 5614 pages, macro leakage-at-bulb KYURUZU (Macromolecules) 1995, 28 volumes, 7901 pages, Science (Science) 1996, 272 volumes, 28 volumes, 1721 etc. pages, etc. will be mentioned in 866 pages, WO 96/No. 30421 official report, WO 97/No. 18247 official report or Sawamoto et al., and macro leakage-at-bulb KYURUZU (Macromolecules) 1995.

[0022] In this atomic migration radical polymerization, an organic halogenide especially the organic halogenide (for example, the carbonyl compound which has a halogen in an alpha position and the compound which has a halogen in the benzylic position) which has reactant high carbon-halogen association, or a halogenation sulfonyl compound is used as an initiator.

[0023] In order to obtain the vinyl system polymer of cross-linking using this polymerization method, the organic halogenide which has two or more start points, or a halogenation sulfonyl compound is used as an initiator. As those examples, o-, m-, p-XCH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>X, o-, m-, p-CH<sub>3</sub>C(H)(X)-C<sub>6</sub>H<sub>4</sub>-C(H)(X)CH<sub>3</sub>, o-, m-, and p-(CH<sub>3</sub>)<sub>2</sub>C(X)-C<sub>6</sub>H<sub>4</sub>-C(X)(CH<sub>3</sub>) -- two (C<sub>6</sub>H<sub>4</sub> show a phenylene group among the above-mentioned formula.) X shows chlorine, a bromine, or iodine.

RO -- 2 C-C(H)(X)-(CH<sub>2</sub>)<sub>n</sub>-C(H)(X)-CO<sub>2</sub>R -- RO<sub>2</sub> C-C(CH<sub>3</sub>)(X)-(CH<sub>2</sub>)<sub>n</sub>-C(CH<sub>3</sub>)(X)-CO<sub>2</sub>R, RC(O)-C(H)(X)-(CH<sub>2</sub>)<sub>n</sub>-C(H)(X)-C(O)R and RC(O)-C(CH<sub>3</sub>)(X)-(CH<sub>2</sub>)<sub>n</sub>-C(CH<sub>3</sub>)(X)-C(O)R (R shows the alkyl group, aryl group, or aralkyl radical of carbon numbers 1-20 among the above-mentioned formula.) n expresses the integer of 0-20 and X shows chlorine, a bromine, and iodine.

XCH<sub>2</sub>-C(--O--)CH<sub>2</sub>--two--X--H--three--C-C(--H--)--(--X--)C(--O--)C(--H--)--(--X--)CH<sub>2</sub>--three--two(H<sub>3</sub>C)--C(--X--)C(--O--)C(--X--)(CH<sub>3</sub>)--two--C--six--H--five--C(--H--)--(--X--)CH<sub>2</sub>--n-C(--H--)--(--X--)C--six--H--five (among the above-mentioned formula) X expresses chlorine, a bromine, or iodine and n shows the integer of 0-20.

XCH<sub>2</sub>CO<sub>2</sub>-(CH<sub>2</sub>)<sub>n</sub>-OCOCH<sub>2</sub>X, CH<sub>3</sub>C(H)(X)CO<sub>2</sub>-(CH<sub>2</sub>)<sub>n</sub>-OCOC(H)(X)CH<sub>3</sub>, and 2(CH<sub>3</sub>)C(X)CO<sub>2</sub>-(CH<sub>2</sub>)<sub>n</sub>-OCOC(X)(CH<sub>3</sub>)--two (n shows the integer of 1-20 among the above-mentioned formula.) -- XCH<sub>2</sub>--two--C(--O--)C(--O--)CH<sub>2</sub>--two--X--CH<sub>2</sub>--three--C(--H--)--(--X--)C(--O--)C(--O--)C(--H--)--(--X--)CH<sub>2</sub>--three--two(CH<sub>3</sub>)--C(--X--)C(--O--)C(--O--)C(--X--)(CH<sub>3</sub>)--two--o-m-p-XCH<sub>2</sub>--two--CO--two--C--six--H--four--OCOCH<sub>2</sub>--2Xo-m-p-CH<sub>2</sub>--three--C(--H--)--(--X--)CO--two--C--six--H--four--OCOC--(--H--)--(--X--)CH<sub>2</sub>--three--o-m-p-(CH<sub>3</sub>)--two--C(--X--)CO--two--C--six--H--four--OCOC--(--X--)(CH<sub>3</sub>)--two--o-m-p-XSO--two--C--six--H--four--SO--two--X (the inside of the above-mentioned formula, and X--chlorine and a bromine--) or iodine is shown.

Although not limited especially as a transition metal complex used as a polymerization catalyst, it is the metal complex complex which uses the 7th group of the periodic table, eight groups, nine groups, ten groups, or 11 group element as a central metal preferably. Furthermore, as a desirable thing, the complex of zerovalent copper, univalent copper, a divalent ruthenium, divalent iron, or divalent nickel is mentioned. Especially, a copper complex is desirable. a univalent copper compound is illustrated concretely -- if it becomes -- a cuprous chloride and bromination -- they are the first copper, a cuprous iodide, a cuprous cyanide, a cuprous oxide, the first copper of perchloric acid, etc. When using a copper compound, in order to raise catalytic activity, ligands, such as polyamine, such as 2,2'-bipyridyl and its derivative, 1, 10-phenanthroline and its derivative, tetramethylethylenediamine, pentamethyl diethylenetriamine, and a hexa methyl tris (2-aminoethyl) amine, are added. Moreover, the tris triphenyl phosphine complex (RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>) of divalent ruthenium chloride is also suitable as a catalyst. When using a ruthenium compound as a catalyst, aluminum alkoxides are added as an activator. Furthermore, the bis-triphenyl phosphine complex (FeCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>) of divalent iron, the bis-triphenyl phosphine complex (NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>) of divalent nickel, and the bis-tributyl phosphine complex (NiBr<sub>2</sub>(PBu<sub>3</sub>)<sub>2</sub>) of divalent nickel are also suitable as a catalyst.

[0024] It is not limited especially as a monomer of the vinyl system used in this polymerization, but all the already illustrated things can be used suitably.

[0025] The above-mentioned polymerization reaction can also be performed in the various following solvents, although a non-solvent is also possible. It is not limited especially as a solvent. For example, hydrocarbon system solvent; diethylether, such as benzene and toluene, Ether system solvents, such as a tetrahydrofuran, diphenyl ether, an anisole, and dimethoxybenzene; A methylene chloride, Halogenated hydrocarbon system solvents, such as chloroform and a chlorobenzene; An acetone, Ketone solvent, such as a methyl ethyl ketone and methyl isobutyl ketone; A methanol, Ethanol, propanol, isopropanol, n-butyl alcohol, Alcoholic solvent, such as tert-butyl alcohol; carbonate system solvents, such as ester solvent; ethylene carbonate, such as nitril system solvent; ethyl acetate, such as an acetonitrile, propionitrile, and a benzonitrile, and butyl acetate, and propylene carbonate, etc. are mentioned. Even when these are independent, they are good, and they may use two or more sorts together. Moreover, a polymerization can be performed also in an emulsion system or the system through supercritical fluid CO<sub>2</sub>.

[0026] A polymerization can be performed in 0-200 degrees C, and the range of it is room temperature -150 degree C preferably.

[0027] Although the manufacture approach of a vinyl system polymer of having at least one alkenyl radical shown by the general formula (1) is illustrated concretely and explained in following [A] - [C], it is not limited to these.

[A] How to introduce a direct alkenyl radical into a polymer principal chain, in case a vinyl system polymer is compounded according to a radical polymerization.

[B] How to permute this halogen by the alkenyl radical content functional group using the vinyl system polymer which has at least one halogen expressed with a general formula (2).

[C] How to permute this hydroxyl group by the alkenyl radical content functional group using the vinyl system polymer which has at least one hydroxyl group.

[0028] Although not limited especially as an approach of introducing a direct alkenyl radical into the polymer principal chain of the above-mentioned synthesis method [A], the approach of [A-a] specifically described below - [A-b] etc. can be mentioned.

[0029] [A-a] The approach to which the compound it has a compound and the alkenyl radical of polymerization nature and the low alkenyl radical of polymerization nature in the monad expressed with the following general formula (9) etc. with a predetermined vinyl system monomer in case a vinyl system polymer is compounded according to a living radical polymerization is also made to react.



Among {type, R<sub>1</sub> expresses hydrogen or a methyl group, and even if mutually the same, it may differ. R<sub>8</sub> shows -C(O) O- (ester group) or o-, m-, or p-phenylene group. R<sub>9</sub> shows the divalent organic radical of the carbon numbers 1-20 which may have direct coupling or one or more ether linkage. As for the thing of an ester group, as for the thing of a phenylene group, R<sub>8</sub> is [ an acrylate (meta) system compound and R<sub>8</sub> ] the compounds of a styrene system. }

Especially as R<sub>9</sub> in the above-mentioned general formula (9), although not limited, an alkylene group including ether linkage, such as aralkyl radical; -CH<sub>2</sub>CH<sub>2</sub>-O-CH<sub>2</sub>-, such as alkylene group; o-, such as methylene, ethylene, and a propylene, m-, and p-phenylene group; benzyl, and -O-CH<sub>2</sub>-, etc. is mentioned, for example.

[0030] Also in the compound of the above-mentioned general formula (9), the following [ point / that acquisition is easy ] are desirable.

H<sub>2</sub> C=C(H) C(O) O(CH<sub>2</sub>) n-CH=CH<sub>2</sub>, H<sub>2</sub> C=C(CH<sub>3</sub>) C(O) O(CH<sub>2</sub>) n-CH=CH<sub>2</sub> (in each above-mentioned formula, n shows the integer of 0-20.)

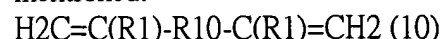
H<sub>2</sub> C=C(H) C(O) O(CH<sub>2</sub>) n-O-(CH<sub>2</sub>) mCH=CH<sub>2</sub>, H<sub>2</sub> C=C(CH<sub>3</sub>) C(O) O(CH<sub>2</sub>) n-O-(CH<sub>2</sub>) mCH=CH<sub>2</sub> (in each above-mentioned formula, n shows the integer of 1-20 and m shows the integer of 0-20.)

o-, m-, p-divinylbenzene, o-, m-, p-H<sub>2</sub>C=CH-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>CH=CH<sub>2</sub>, o-, m-, p-H<sub>2</sub>C=CH-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>-C(CH<sub>3</sub>)=CH<sub>2</sub>, o-, m-, p-H<sub>2</sub>C=CH-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>, o-, m-, p-H<sub>2</sub>C=CH-C<sub>6</sub>H<sub>4</sub>-OCH<sub>2</sub>CH=CH<sub>2</sub>, o-, m-, p-H<sub>2</sub>C=CH-C<sub>6</sub>H<sub>4</sub>-OCH<sub>2</sub>-C(CH<sub>3</sub>)=CH<sub>2</sub>, o-, m-, p-H<sub>2</sub>C=CH-C<sub>6</sub>H<sub>4</sub>-OCH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>, o-, m-, p-H<sub>2</sub>C=C(CH<sub>3</sub>)-C<sub>6</sub>H<sub>4</sub>-C=CH<sub>2</sub>, o-, m-, p-H<sub>2</sub>C=C(CH<sub>3</sub>)(CH<sub>3</sub>)-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>CH=CH<sub>2</sub>, o-, m-, p-H<sub>2</sub>C=C(CH<sub>3</sub>)-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>C(CH<sub>3</sub>)=CH<sub>2</sub>, o-, m-, p-H<sub>2</sub>C=C(CH<sub>3</sub>)-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>, o-, m-, p-H<sub>2</sub>C=C(CH<sub>3</sub>)-C<sub>6</sub>H<sub>4</sub>-OCH<sub>2</sub>CH=CH<sub>2</sub>, o-, m-, p-H<sub>2</sub>C=C(CH<sub>3</sub>)-C<sub>6</sub>H<sub>4</sub>-OCH<sub>2</sub>-C(CH<sub>3</sub>)=CH<sub>2</sub>, o-, m-, p-H<sub>2</sub>C=C(CH<sub>3</sub>)-C<sub>6</sub>H<sub>4</sub>-OCH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub> (in each above-mentioned formula) C<sub>6</sub>H<sub>4</sub> show a phenylene group.

In addition, although there is especially no limit as a stage to which the compound having the alkenyl radical of the above-mentioned polymerization nature and the low alkenyl radical of polymerization nature is made to react, in a living radical polymerization, it is desirable to make it react as the 2nd monomer after reaction termination of the telophase of a polymerization reaction or a predetermined monomer.

[0031] [A-b] The approach to which the compound which has at least two low alkenyl radicals of polymerization nature as the 2nd monomer after reaction termination of the telophase of a polymerization reaction or a predetermined monomer is made to react in case a vinyl system polymer is compounded according to a living radical polymerization.

[0032] Although not limited especially as such a compound, the compound shown in a general formula (10) is mentioned.



(Among the formula, R<sub>1</sub> expresses hydrogen or a methyl group, and even if mutually the same, it may differ.) R<sub>10</sub> shows the divalent organic radical of the carbon numbers 1-20 which may include one or more ether linkage.

Although not limited especially as a compound shown in the above-mentioned general formula (10), since it says that acquisition is easy, 1, 5-hexadiene, 1, 7-OKUTA diene, 1, and 9-deca diene is desirable.

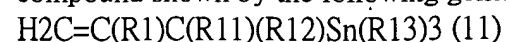
[0033] In the synthetic approach of a vinyl system polymer by introducing a direct alkenyl radical into the polymer principal chain of the above-mentioned synthesis method [A] of having at least one alkenyl radical, the approach of the point that control of the alkenyl radical introduced into per monad is easier to [A-b] is desirable.

[0034] The atomic migration radical polymerization method of the synthesis method of the vinyl system polymer which has at least one halogen expressed with the general formula (2) in the above-mentioned synthesis method [B] is desirable. Although not limited especially as an approach of permuting the halogen of this polymer by the alkenyl radical content functional group, the approach of [B-a] specifically described below - [B-d] etc. can be mentioned.

[0035] [B-a] How to make various kinds of organometallic compounds which have an alkenyl radical act on the vinyl system polymer which has at least one halogen expressed with a general formula (2), and to permute a halogen.

[0036] As such an organometallic compound, an organic lithium, organic sodium, an organic potassium, organic magnesium, organic tin, organic silicon, organic zinc, organic copper, etc. are mentioned. It reacts to the halogen and selection target of the above-mentioned general formula (2) especially, and organic tin and an organocopper compound are desirable at the point that reactivity with a carbonyl group is low.

[0037] As an organic tin compound which has an alkenyl radical, although there is especially no limit, the compound shown by the following general formula (11) is desirable.



(R<sub>1</sub> is the same as that of what was mentioned above among a formula.) R<sub>11</sub> and R<sub>12</sub> express hydrogen or the alkyl group of carbon numbers 1-10, the aryl group of carbon numbers 6-10, or the aralkyl radical of carbon numbers 7-10, and even if these are mutually the same, they may differ. R<sub>13</sub> shows the alkyl group, aryl group, or aralkyl radical of carbon numbers 1-10.

If the example of the organic tin compound of the above-mentioned general formula (11) is shown, allyl

compound tributyl tin, allyl compound trimethyl tin, ant RUTORI (n-octyl) tin, ant RUTORI (cyclohexyl) tin, etc. will be illustrated. As an organocopper compound which has an alkenyl radical, a divinyl copper lithium, a diaryl copper lithium, a JIISO propenyl copper lithium, etc. are illustrated.

[0038] [B-b] How to make the stabilization carbanion which has the alkenyl radical expressed with the following general formula (12) etc. react to the vinyl system polymer which has at least one halogen expressed with a general formula (2), and to permute a halogen by it.

$M^+C-(R_6)(R_7)-R_5-C(R_1)=CH_2$  (12)

( $R_1$ ,  $R_5$ ,  $R_6$ , and  $R_7$  are the same as that of what was mentioned above among a formula.)  $M^+$  shows alkali-metal ion or the 4th class ammonium ion.

As alkali-metal ion, a lithium ion, sodium ion, and potassium ion are mentioned as the 4th class ammonium ion, and tetramethyl ammonium ion, tetraethyl ammonium ion, trimethyl benzyl ammonium ion, trimethyl dodecyl ammonium ion, tetrabutyl ammonium ion, etc. are mentioned as an example again.

[0039] The carbanion of the above-mentioned general formula (12) can make a basic compound able to act to the precursor, and can be obtained by drawing out an activity proton.

[0040] The following compounds can be illustrated as a precursor compound of the carbanion of a general formula (12).

$H_2C=CH-CH_2$ ,  $H_2C=CH-CH(CO_2CH_3)_2$ ,  $H_2C=CH-(CO_2C_2H_5)_nCH(CH_2)_2$ ,  $H_2C=CH-(CO_2CH_3)_nCH(CH_2)_2$ , o-, m-, p- $H_2C=CH-C_6H_4-CH(CO_2CH_3)_2$ , o-, m-, p- $H_2C=CH-C_6H_4-CH(CO_2C_2H_5)_2$ , o-, m-, p- $H_2C=CH-C_6H_4-CH_2CH(CO_2C_2H_5)_2$ , o-, m-, p- $H_2C=CH-C_6H_4-CH_2CH(CO_2C_2H_5)_2$ ,  $H_2C=CH-CH(C(O)CH_3)(CO_2C_2H_5)$ ,  $(CO_2CH_3)_2H_2C=CH-(CH_2)_nCH(C(O)CH_3)(CO_2C_2H_5)$ , o-, m-, p- $H_2C=CH-C_6H_4-CH(C(O)CH_3)(CO_2C_2H_5)$ , o-, m-, p- $H_2C=CH-C_6H_4-CH_2CH(C(O)CH_3)(CO_2C_2H_5)$ ,  $H_2C=CH-CH(O)(C(O)CH_3)_2$ ,  $H_2C=CH-nCH(C(O)CH_3)_2$ , o-, m-, p- $H_2C=CH-C_6H_4-CH(C(O)CH_3)_2$ , o-, m-, p- $H_2C=CH-C_6H_4-CH_2CH(C(O)CH_3)_2$ ,  $H_2C=CH-CH(CN)$ ,  $(CO_2C_2H_5)$ ,  $(CH_2)_nH_2C=CH-(CH_2)_nCH(CN)$ ,  $(CO_2C_2H_5)$ , o-, m-, p- $H_2C=CH-C_6H_4-CH(CN)$ ,  $(CO_2C_2H_5)$ , o-, m-, p- $H_2C=CH-C_6H_4-CH_2CH(CN)$ ,  $(CO_2C_2H_5)$ ,  $H_2C=CH-CH(CN)_2$ ,  $H_2C=CH-nCH(CH_2)(CN)_2$ , o-, m-, p- $H_2C=CH-C_6H_4-CH(CN)_2$ , o-, m-, p- $H_2C=CH-C_6H_4-CH_2CH(CN)_2$ ,  $H_2C=CH-(CH_2)_nNO_2$ , o-, m-, p- $H_2C=CH-C_6H_4-CH_2CH_2NO_2$ ,  $H_2C=CH-CH(C_6H_5)(CO_2C_2H_5)$ ,  $H_2C=CH-(CH_2)_nCH(C_6H_5)(CO_2C_2H_5)$ , o-, m-, p- $H_2C=CH-C_6H_4-CH(C_6H_5)(CO_2C_2H_5)$ , o-, m-, p- $H_2C=CH-C_6H_4-CH_2CH(C_6H_5)(CO_2C_2H_5)$

(n shows the integer of 1-10 among the above-mentioned formula.)

In order to draw out a proton from the above-mentioned compound and to consider as the carbanion of a general formula (12), various kinds of basic compounds are used. The following compounds can be illustrated as these basic compounds. Alkali metal, such as sodium, a potassium, and a lithium; Sodium methoxide, A potassium methoxide, a lithium methoxide, a sodium ethoxide, Potassium ethoxide, lithium ethoxide, sodium-tert-butoxide, Metal alkoxides, such as potassium-tert-butoxide; A sodium carbonate, Carbonates, such as potassium carbonate, a lithium carbonate, and a sodium hydrogencarbonate; A sodium hydroxide, Hydroxides, such as a potassium hydroxide; Sodium hydride, potassium hydride, Hydride; n-butyl lithium, such as methyl lithium and an ethyl lithium, Organic metal; ammonia, such as tert-butyl lithium, a lithium diisopropyl amide, and lithium hexa methyl JISHIRAJIDO; A trimethylamine, Alkylamines, such as triethylamine and tributylamine; Tetramethylethylenediamine, Polyamine, such as pentamethyl diethylenetriamine; \*\*\*\*\* for the equivalent or small excessive amounts of the amount of the basic compounds used, such as pyridine system compounds, such as a pyridine and picoline, is good to a precursor, and it is 1-1.2Eq preferably.

[0041] Quarternary ammonium salt can also be used as the above-mentioned carbanion. In this case, what is the alkali-metal salt of a carboxylic-acid compound is prepared, and it is obtained by making the 4th class ammonium halide act on this. As the 4th class ammonium halide, tetramethyl ammonium halide, tetraethyl ammonium halide, trimethyl benzyl ammonium halide, trimethyl dodecyl ammonium halide, tetrabutyl ammonium halide, etc. are illustrated.

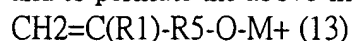
[0042] As a solvent used in case the above-mentioned precursor compound and a basic compound are made to react For example, hydrocarbon system solvents, such as benzene and toluene; Diethylether, Ether system solvents, such as a tetrahydrofuran, diphenyl ether, an anisole, and dimethoxybenzene; A methylene chloride, Halogenated hydrocarbon system solvents, such as chloroform; An acetone, a methyl ethyl ketone, Ketone solvent, such as methyl isobutyl ketone; A methanol, ethanol, Alcoholic solvent, such as propanol, isopropanol, n-butyl alcohol, and tert-butyl alcohol; An acetonitrile, Nitril system solvents, such as propionitrile and a benzonitrile; Ethyl acetate, Ester solvent, such as butyl acetate; sulfoxide system solvents [ , such as amide system solvent; dimethyl sulfoxide, ], such as carbonate system solvent; dimethylformamides, such as ethylene carbonate and propylene carbonate, and dimethylacetamide, etc. are mentioned. Independent or two sorts or more can be mixed and used for these.

[0043] By making a basic compound act on the above-mentioned precursor, the carbanion expressed with a general formula (12) is prepared, and the vinyl system polymer which has at the end the alkenyl radical expressed with the target general formula (1) can be obtained by making it react with the vinyl system polymer which has the halogen end of a general formula (2).

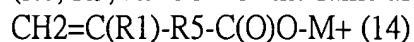
[0044] [B-c] The electrophilicity compound which a metal simple substance or an organometallic compound is made to act on the vinyl system polymer which has at least one halogen expressed with a general formula (2), considers as an ENORETO anion, and has an alkenyl radical after an appropriate time, and the approach of making it react.

[0045] Especially zinc is desirable to a lifting in respect of a pile for side reaction which the ENORETO anion to generate attacks other ester groups as a metal simple substance, or it transfers. Various kinds of things can be used as an electrophilicity compound which has an alkenyl radical. For example, they are the alkenyl radical content compound which has a leaving group like a halogen or an acetyl group, the carbonyl compound which has an alkenyl radical, the isocyanate compound which has an alkenyl radical, the acid halide which has an alkenyl radical. If the alkenyl radical content compound which has a leaving group like a halogen or an acetyl group among these is used, since any atoms other than carbon will not be introduced into a principal chain and the weatherability of a vinyl system polymer will not be lost, it is desirable.

[0046] [B-d] How to make the alkenyl radical content carboxylate anion expressed with an alkenyl radical content oxy-anion or the following general formula (14) expressed with the following general formula (13) etc. by the vinyl system polymer which has at least one halogen expressed with a general formula (2) react, and to permute the above-mentioned halogen by the alkenyl radical content substituent.



(R<sub>1</sub>, R<sub>5</sub>, and M<sup>+</sup> are the same as that of what was mentioned above among a formula.)



(R<sub>1</sub>, R<sub>5</sub>, and M<sup>+</sup> are the same as that of what was mentioned above among a formula.)

As a precursor compound of the oxy-anion expressed with a general formula (13) and (14), the following compound: H<sub>2</sub> C=CH-CH<sub>2</sub>-OH(s), H<sub>2</sub> C=CH-CH(CH<sub>3</sub>)-OH, H<sub>2</sub> C=C(CH<sub>3</sub>)-CH<sub>2</sub>-OH, H<sub>2</sub>C=CH-(CH<sub>2</sub>)<sub>n</sub>-OH (n shows the integer of 2-20.) H<sub>2</sub> C=CH-CH<sub>2</sub>-O-(CH<sub>2</sub>)<sub>2</sub>-OH, H<sub>2</sub> C=CH-C(O) O-(CH<sub>2</sub>)<sub>2</sub>-OH, H<sub>2</sub> C=C(CH<sub>3</sub>)-C(O) O-(CH<sub>2</sub>)<sub>2</sub>-OH, o-, m-, p-H<sub>2</sub> C=CH-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>-OH, o-, m-, p-H<sub>2</sub> C=CH-CH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>-OH, Alcoholic hydroxyl-group-containing-compound; o-, such as o-, m-, and p-H<sub>2</sub> C=CH-CH<sub>2</sub>-O-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>-OH, m-, p-H<sub>2</sub> C=CH-C<sub>6</sub>H<sub>4</sub>-OH, Phenol nature hydroxyl-group-containing-compound; H<sub>2</sub> C=CH-C(O)-OH(s), such as o-, m-, p-H<sub>2</sub> C=CH-CH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-OH, o-, m-, and p-H<sub>2</sub> C=CH-CH<sub>2</sub>-O-C<sub>6</sub>H<sub>4</sub>-OH, H<sub>2</sub> C=C(CH<sub>3</sub>)-C(O)-OH, H<sub>2</sub> C=CH-CH<sub>2</sub>-C(O)-OH, H<sub>2</sub>C=CH-(CH<sub>2</sub>)<sub>n</sub>-C(O)-OH (n shows the integer of 2-20.) H<sub>2</sub> C=CH-(CH<sub>2</sub>)<sub>n</sub>-OC(O)-(CH<sub>2</sub>)<sub>m</sub>-C(O)-OH (m and n) the same -- or it differs and the integer of 0-19 is shown. o-, m-, p-H<sub>2</sub> C=CH-C<sub>6</sub>H<sub>4</sub>-C(O)-OH, o-, m-, p-H<sub>2</sub> C=CH-CH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-C(O)-OH, o-, m-, p-H<sub>2</sub> C=CH-CH<sub>2</sub>-O-C<sub>6</sub>H<sub>4</sub>-C(O)-OH, o-, m-, p-H<sub>2</sub> C=CH-(CH<sub>2</sub>)<sub>n</sub>-OC(O)-C<sub>6</sub>H<sub>4</sub>-C(O)-OH (n shows the integer of 0-13.) etc. -- carboxyl group content compound; etc. is mentioned.

[0047] All the basic compounds used in case various kinds of basic compounds are used and the carbanion of

the above-mentioned general formula (12) is prepared as the example, in order to draw out a proton from the above-mentioned compound and to consider as the above-mentioned general formula (13) or the anion of (14) are used suitably. Moreover, all the things used in case carbanion is prepared also about a reaction solvent are used suitably.

[0048] In the above-mentioned synthesis method [B], since an alkenyl radical can be introduced by the high ratio, the approach of introducing an alkenyl radical is desirable by changing the halogen of the vinyl system polymer which has at least one halogen expressed with the general formula (2) obtained in the organic halogenide or the halogenation sulfonyl compound by the atomic migration radical polymerization method using an initiator and a transition metal complex as a catalyst by the approach of [B-d]. In the approach of [B-d], the approach to which the alkenyl radical content carboxylate anion expressed with a general formula (14) etc. is made to react is more desirable.

[0049] In the manufacturing method of the vinyl system polymer characterized by using the atomic migration radical polymerization method which makes an initiator an organic halogenide or a halogenation sulfonyl compound, and carries out the polymerization of the vinyl system monomer by making a transition metal complex into a catalyst, if the organic halogenide which has an alkenyl radical is used as an initiator, the vinyl system polymer with which it has an alkenyl radical at the piece end, and other ends have the structure of the above-mentioned general formula (2) can be obtained. Thus, if the halogen of the halt end of the polymer obtained is changed into an alkenyl radical content substituent, the vinyl system polymer which has an alkenyl radical in both ends can be obtained. The already indicated approach can be used as the conversion approach.

[0050] Although there is especially no limit as an organic halogenide which has an alkenyl radical, what has the structure shown in the following general formula (15), for example is illustrated.

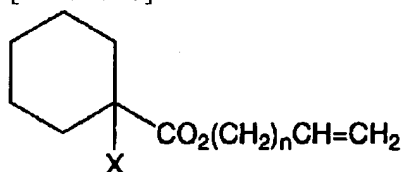
R14R15C(X)-R16-R9-C(R1)=CH<sub>2</sub> (15)

R1, R9, and X are the same as that of what was mentioned above among {type. R14 and R15 show what was mutually connected in hydrogen or the alkyl group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, the aralkyl radical of carbon numbers 7-20, or the other end. R16 shows -C(O) O- (ester group), -C(O)- (keto radical) or o-, m-, and p-phenylene group. }

As an example of an organic halogenide of having the alkenyl radical expressed with a general formula (15)

XCH<sub>2</sub>C(O) O(CH<sub>2</sub>)<sub>n</sub>CH=CH<sub>2</sub>, Hthree cc(H) (X) C(O) O(CH<sub>2</sub>)<sub>n</sub>CH=CH<sub>2</sub>, 2(H3C) C(X) C(O) O(CH<sub>2</sub>)<sub>n</sub>CH=CH<sub>2</sub>, CH<sub>3</sub>CH<sub>2</sub>C(H) (X) C(O) O(CH<sub>2</sub>)<sub>n</sub>CH=CH<sub>2</sub>, [0051]

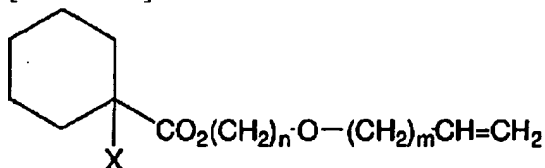
[Formula 1]



(In each above-mentioned formula, X shows chlorine, a bromine, or iodine.) n shows the integer of 0-20.

XCH<sub>2</sub>C(O) O nO (CH<sub>2</sub>)<sub>m</sub>CH=CH<sub>2</sub>, H3cc (CH<sub>2</sub>) (H) (X) C(O) O(CH<sub>2</sub>)<sub>n</sub>O(CH<sub>2</sub>)<sub>m</sub>CH=CH<sub>2</sub>, 2(H3C) C (X) C(O) O(CH<sub>2</sub>)<sub>n</sub>O(CH<sub>2</sub>)<sub>m</sub>CH=CH<sub>2</sub>, CH<sub>3</sub>CH<sub>2</sub>C(H) (X) C(O) O(CH<sub>2</sub>)<sub>n</sub>O(CH<sub>2</sub>)<sub>m</sub>CH=CH<sub>2</sub>, [0052]

[Formula 2]



(In each above-mentioned formula, X shows chlorine, a bromine, or iodine.) n shows the integer of 1-20 and m shows the integer of 0-20.

o, m, p-XCH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-(CH<sub>2</sub>)<sub>n</sub>-CH=CH<sub>2</sub>, o and m, p-CH<sub>3</sub>C(H) (X)-C<sub>6</sub>H<sub>4</sub>-(CH<sub>2</sub>)<sub>n</sub>-CH=CH<sub>2</sub>, o and m, and p-CH<sub>3</sub> -- CH<sub>2</sub>C(H) (X)-C<sub>6</sub>H<sub>4</sub>-(CH<sub>2</sub>)<sub>n</sub>-CH=CH<sub>2</sub> (in each above-mentioned formula, X shows chlorine, a bromine, or iodine.) n shows the integer of 0-20.

o, m, p-XCH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>- n-O- (CH<sub>2</sub>) (CH<sub>2</sub>) m-CH=CH<sub>2</sub>, o and m, and p-CH<sub>3</sub> -- C(H) (X)-C<sub>6</sub>H<sub>4</sub>-(CH<sub>2</sub>)<sub>n</sub>-O-(CH<sub>2</sub>) m-CH=CH<sub>2</sub>, o and m, and p-CH<sub>3</sub>CH<sub>2</sub> -- C(H) (X)-C<sub>6</sub>H<sub>4</sub>-(CH<sub>2</sub>)<sub>n</sub>-O-(CH<sub>2</sub>) m-CH=CH<sub>2</sub> (each above-mentioned formula -- setting -- X -- chlorine --) A bromine or iodine is shown. n expresses the integer of 1-20 and m shows the integer of 0-20.

o, m, and p-XCH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-O-(CH<sub>2</sub>)<sub>n</sub>-CH=CH<sub>2</sub>, o and m, and p-CH<sub>3</sub> -- C(H) (X)-C<sub>6</sub>H<sub>4</sub>-O-(CH<sub>2</sub>)<sub>n</sub>-CH=CH<sub>2</sub>, o and m, and p-CH<sub>3</sub>CH<sub>2</sub> -- C(H) (X)-C<sub>6</sub>H<sub>4</sub>-O-(CH<sub>2</sub>)<sub>n</sub>-CH=CH<sub>2</sub> (in each above-mentioned formula) X expresses chlorine, a bromine, or iodine and n shows the integer of 0-20.

o, m, and p-XCH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-O- n-O- (CH<sub>2</sub>) (CH<sub>2</sub>) m-CH=CH<sub>2</sub>, o and m, p-CH<sub>3</sub>C(H) (X)-C<sub>6</sub>H<sub>4</sub>-O-(CH<sub>2</sub>)<sub>n</sub>-O-(CH<sub>2</sub>) m-CH=CH<sub>2</sub>, o and m, and p-CH<sub>3</sub>CH<sub>2</sub>C -- (H) (X)-C<sub>6</sub>H<sub>4</sub>-O-(CH<sub>2</sub>)<sub>n</sub>-O- (CH<sub>2</sub>) -- m-CH=CH -- two (in each above-mentioned formula) X shows chlorine, a bromine, or iodine. n expresses the integer of 1-20 and m shows the integer of 0-20.

The compound further shown by the general formula (16) as an organic halogenide which has an alkenyl radical is mentioned.

H<sub>2</sub>C=C(R<sub>1</sub>)-R<sub>9</sub>-C(R<sub>14</sub>)(X)-R<sub>17</sub>-R<sub>15</sub> (16)

R<sub>1</sub>, R<sub>9</sub>, R<sub>14</sub>, R<sub>15</sub>, and X are the same as that of what was mentioned above among {type. R<sub>17</sub> shows direct coupling, -C(O) O- (ester group), -C(O)- (keto radical) or o-, m-, and p-phenylene group. }

Although R<sub>9</sub> is direct coupling or the divalent organic radical (one or more ether linkage may be included) of carbon numbers 1-20, when it is direct coupling, the vinyl group has combined with the carbon which has combined the halogen, and it is an allyl halide ghost. In this case, since carbon-halogen association is activated by the contiguity vinyl group, there may not necessarily be need of having C(O) O set, a phenylene group, etc. as R<sub>17</sub>, and may be direct coupling. When R<sub>9</sub> is not direct coupling, in order to activate carbon-halogen association, as R<sub>17</sub>, O sets, a C(O) C (O) radical, and a phenylene group are desirable.

[0053] The compound of the above-mentioned general formula (16) can specifically illustrate the following compound.

CH<sub>2</sub>=CHCH<sub>2</sub>X, CH<sub>2</sub>=C(CH<sub>3</sub>) CH<sub>2</sub>X, CH<sub>2</sub>=CHC (H) (X) CH<sub>3</sub>, CH<sub>2</sub>=C C (CH<sub>3</sub>) (H) (X) CH<sub>3</sub>, CH<sub>2</sub>=CHC (X) (CH<sub>3</sub>)<sub>2</sub>, CH<sub>2</sub>=CHC(H) (X) C<sub>2</sub>H<sub>5</sub>, CH<sub>2</sub>=CHC(H) (X) CH (CH<sub>3</sub>)<sub>2</sub>, CH<sub>2</sub>=CHC(H) (X) C<sub>6</sub>H<sub>5</sub>, CH<sub>2</sub>=CHC (H) (X) CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, CH<sub>2</sub>=CHCH<sub>2</sub>C(H) (X)-CO<sub>2</sub>R, CH<sub>2</sub>=CH(CH<sub>2</sub>)<sub>2</sub>C(H) (X)-CO<sub>2</sub>R, CH<sub>2</sub>=CH(CH<sub>2</sub>)<sub>3</sub>C(H) (X)-CO<sub>2</sub>R, CH<sub>2</sub>=CH(CH<sub>2</sub>)<sub>8</sub>C(H) (X)-CO<sub>2</sub>R, CH<sub>2</sub>=CHCH<sub>2</sub>C(H) (X)-C<sub>6</sub>H<sub>5</sub>, CH<sub>2</sub>=CH(CH<sub>2</sub>)<sub>2</sub>C(H) (X)-C<sub>6</sub>H<sub>5</sub>, and CH<sub>2</sub>=CH(CH<sub>2</sub>)<sub>3</sub>C(H) (X)-C<sub>6</sub>H<sub>5</sub> (each above-mentioned formula -- setting -- X -- chlorine and a bromine --) Or iodine is shown. R shows the alkyl group of carbon numbers 1-20, an aryl group, and an aralkyl radical.

The halogenation sulfonyl compound which has an alkenyl radical can specifically illustrate the following compound.

o-, m-, p-CH<sub>2</sub>=CH-(CH<sub>2</sub>)<sub>n</sub>-C<sub>6</sub>H<sub>4</sub>-SO<sub>2</sub>X, o-, m-, p-CH<sub>2</sub>=CH-(CH<sub>2</sub>)<sub>n</sub>-O-C<sub>6</sub>H<sub>4</sub>-SO<sub>2</sub>X (in each above-mentioned formula, X shows chlorine, a bromine, or iodine.) n shows the integer of 0-20.

If the organic halogenide which has an alkenyl radical, or a halogenation sulfonyl compound is used as an initiator, the polymer of a halogen end in which a piece end is shown by the alkenyl radical and other ends are shown by the above-mentioned general formula (2) can be obtained. The vinyl system polymer which can permute the halogen expressed with the general formula (2) of this polymer and which has an alkenyl radical at the end also the same or by carrying out coupling of the halogen ends using the compound which has a total of two or more different functional groups can be obtained.

[0054] Although there is especially no limit as a thing which can permute an end halogen and which has a total of the same or two or more different functional groups, polyol, polyamine, polycarboxylic acid, the poly thiols and those salts, an alkali-metal sulfide, etc. are desirable. The following compound can be illustrated as

an example of these compounds.

[0055] Ethylene glycol, 1, 2-propanediol, 1,3-propanediol, 2-methyl-1,3-propanediol, 2, and 2-dimethyl-1,3-propanediol, 1,4-butanediol, 1,3-butanediol, 1, 2-butanediol, 2, 3-butanediol, a pinacol, 1,5-pentanediol, 1, 4-pentanediol, 2, 4-pentanediol, 1,6-hexanediol, 1, 7-heptane diol, 1, 8-octanediol, 1, 9-nonane diol, 1, 10-Deccan diol, 1, 12-dodecane diol, 1, 2-cyclopentane diol, 1, 3-cyclopentane diol, 1, 2-cyclohexane diol, 1, 3-cyclohexane diol, 1, 4-cyclohexane diol, Glycerol, 1 and 2, 4-butane triol, a catechol, resorcinol, A hydroquinone, 1, 2-dihydroxy naphthalene, 1, 3-dihydroxy naphthalene, 1, 5-dihydroxy naphthalene, 2, 6-dihydroxy naphthalene, - biphenol, and 2 and 2 '4, 4'-biphenol, bis(4-hydroxyphenyl) methane, - isopropylidene phenol, and 4 and 4 '3, 3'-(ethylene dioxy) diphenol, alpha and alpha'-dihydroxy-para xylene, 1 and 1, 1-tris (4-hydroxyphenyl) ethane, Polyols, such as pyrogallol, 1 and 2, and 4-benzene triol; It reaches. The alkali-metal salt of the above-mentioned polyol compound; Ethylenediamine, 1, 3-diaminopropane, 1, 2-diaminopropane, 1,4-diaminobutane, 1, 2-diamino-isobutane, 1,5-diaminopentane, 2, and 2-dimethyl-1,3-propanediamine, 1, 6-hexanediamine, 1, 7-heptane diamine, 1, 8-octane diamine, 1, 9-diamino nonane, 1, 10-diamino decane, 1, 12-diamino dodecane, 4 and 4'-methylenebis (cyclohexylamine), 1, 2-diamino cyclohexane, 1, 3-diamino cyclohexane, 1, 4-diamino cyclohexane, 1, 2-phenylenediamine, 1, 3-phenylenediamine, 1, 4-phenylenediamine, Polyamine [, such as alpha and alpha'-diamino-para xylene, ]; and the alkali-metal salt of the above-mentioned polyamine compound; Oxalic acid, A malonic acid, a methylmalonic acid, a dimethyl malonic acid, a succinic acid, a methyl succinic acid, A glutaric acid, an adipic acid, 1, 7-heptane dicarboxylic acid, 1, 8-octane dicarboxylic acid, 1, 9-nonane dicarboxylic acid, 1, 10-Deccan dicarboxylic acid, 1, and 11-undecane dicarboxylic acid, 1, 12-dodecane dicarboxylic acid, 1, 2-cyclopentane dicarboxylic acid, 1, 2-cyclohexane dicarboxylic acid, 1, 3-cyclohexane dicarboxylic acid, 1, 4-cyclohexane dicarboxylic acid, 1 and 3, 5-cyclohexane tricarboxylic acid, A phthalic acid, isophthalic acid, a terephthalic acid, 1 and 2, 3-benzene tricarboxylic acid, Polycarboxylic acid [, such as 1, 2, 4, and 5-benzene tetracarboxylic acid ]; and the alkali-metal salt of the above-mentioned polycarboxylic acid; 1, 2-ethane dithiol, 1, 3-propane dithiol, 1, 4-butane dithiol, 2, 3-butane dithiol, 1, 5-pentane dithiol, 1, 6-hexane dithiol, 1, 7-heptane dithiol, 1, 8-octane dithiol, 1, 9-nonane dithiol, 2-mercapto ethyl ether, Poly thiols [, such as para xylene-alpha and alpha'-dithiol, 1, 2-benzene dithiol 1, 3-benzene dithiol, 1, and 4-benzene dithiol, ]; and the alkali-metal salt of the above-mentioned Pori thiol compounds; a sulfuration lithium, a sodium sulfide, a potassium sulfide.

[0056] In case the above-mentioned polyol, polyamine, polycarboxylic acid, and the poly thiol are used, in order to promote a substitution reaction, a basic compound is used together and what was already illustrated is mentioned as the example.

[0057] Although not limited using the vinyl system polymer which has at least one hydroxyl group of the above-mentioned synthesis method [C] especially as an approach of permuting this hydroxyl group by the alkenyl radical content functional group, the approach of [C-a] specifically described below - [C-d] etc. can be mentioned.

[0058] In addition, the vinyl system polymer which has at least one above-mentioned hydroxyl group can be obtained by the approach of [D-a] - [D-f] mentioned later.

[0059] [C-a] How to make it react with an alkenyl radical content halogenide like an allyl chloride, after making bases, such as a sodium hydroxide and sodium methoxide, act on the hydroxyl group of the vinyl system polymer which has at least one hydroxyl group.

[0060] [C-b] The approach to which the vinyl system polymer and alkenyl radical content isocyanate compounds, such as allyl compound isocyanate, which have at least one hydroxyl group are made to react.

[0061] [C-c] The approach to which the vinyl system polymer which has at least one hydroxyl group under base existence, such as a pyridine, is made to react with alkenyl radical content acid halides, such as acrylic-acid (meta) chloride.

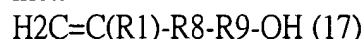
[0062] [C-d] The approach to which the vinyl system polymer and alkenyl radical content carboxylic acids,



such as an acrylic acid, which have at least one hydroxyl group under existence of an acid catalyst are made to react.

[0063] The manufacture approach of a vinyl system polymer of having at least one hydroxyl group used by the approach of [C] is not limited to these approaches, although an approach like [D-a] - [D-f] shown below is illustrated.

[0064] [D-a] The approach to which the compound it has a compound, and the alkenyl radical and hydroxyl group of polymerization nature in the monad expressed with the following general formula (17) etc. in case a vinyl system polymer is compounded according to a living radical polymerization is made to react as the 2nd monomer.

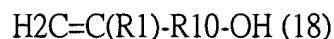


(R<sub>1</sub>, R<sub>8</sub>, and R<sub>9</sub> are the same as that of what was mentioned above among a formula.)

In addition, although there is no limit at the stage to which the compound it has a compound, and the alkenyl radical and hydroxyl group of polymerization nature in a monad is made to react, when it expects a rubber-property especially, it is desirable to make it react as the 2nd monomer after reaction termination of the telophase of a polymerization reaction or a predetermined monomer.

[0065] [D-b] The approach to which the compound which has the low alkenyl radical and low hydroxyl group of polymerization nature in a monad is made to react as the 2nd monomer after reaction termination of the telophase of a polymerization reaction, or a predetermined monomer in case a vinyl system polymer is compounded according to a living radical polymerization.

[0066] Although not limited especially as such a compound, the compound shown in a general formula (18) is mentioned.

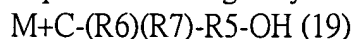


(R<sub>1</sub> and R<sub>10</sub> are the same as that of what was mentioned above among a formula.)

Although not limited especially as a compound shown in the above-mentioned general formula (18), since it says that acquisition is easy, 10-UNDESE Norian, 5-hexenol, and alkenyl alcohol like allyl alcohol are desirable.

[0067] [D-c] How to introduce a hydroxyl group into an end by making the halogen of the vinyl system polymer which has carbon-halogen association expressed with the general formula (2) obtained according to an atomic migration radical polymerization in at least one piece by approach which is indicated by JP,4-132706,A etc. react with hydrolysis or hydroxyl group-containing compound.

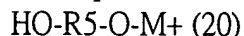
[0068] [D-d] How to make the stabilization carbanion which has a hydroxyl group which is mentioned to a general formula (19) react to the vinyl system polymer which has at least one carbon-halogen association expressed with the general formula (2) obtained according to an atomic migration radical polymerization, and to permute a halogen by it.



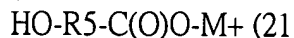
(R<sub>5</sub>, R<sub>6</sub>, and R<sub>7</sub> are the same as that of what was mentioned above among a formula.)

[D-e] How to make the metal simple substance or organometallic compound like zinc act on the vinyl system polymer which has at least one carbon-halogen association expressed with the general formula (2) obtained according to an atomic migration radical polymerization, to prepare an ENORETO anion, and to make aldehydes or ketones react to after an appropriate time.

[0069] [D-f] How to make the hydroxyl-group content carboxylate anion expressed with a hydroxyl-group content oxy-anion or the following general formula (21) expressed with the following general formula (20) etc. by the vinyl system polymer which has at least one halogen expressed with a general formula (2) react, and to permute the above-mentioned halogen by the hydroxyl-group content substituent.



(R<sub>5</sub> and M<sup>+</sup> are the same as that of what was mentioned above among a formula.)

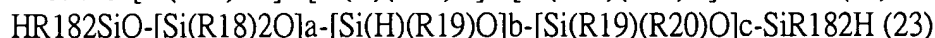
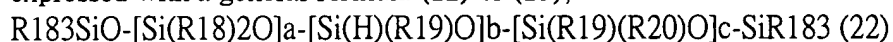


(R5 and M+ are the same as that of what was mentioned above among a formula.)

When a halogen does not participate in the approach of introducing a hydroxyl group like [D-a] - [D-b] in this invention directly, the approach of the point that control is easier to [D-b] is still more desirable.

[0070] Moreover, when introducing a hydroxyl group by changing the halogen of the vinyl system polymer which has at least one carbon-halogen association expressed with a general formula (2) like [D-c] - [D-f], the approach of the point that control is easier to [D-f] is still more desirable.

As a hydrosilyl radical content compound of [hydrosilyl radical content (B) Compound (B) of component] component, there is especially no limit and it can use various kinds of things. Namely, chain-like polysiloxane expressed with a general formula (22) or (23);

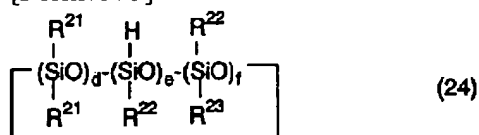


(As for R18 and R19, the alkyl group of carbon numbers 1-6 or a phenyl group, and R20 show the alkyl group or aralkyl radical of carbon numbers 1-10 among a formula.) a shows the integer with which  $0 \leq a \leq 100$  and b fill  $2 \leq b \leq 100$ , and c fills  $0 \leq c \leq 100$ .

Cyclosiloxane expressed with a general formula (24);

[0071]

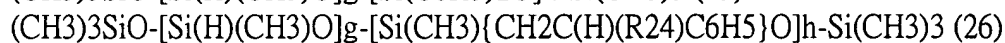
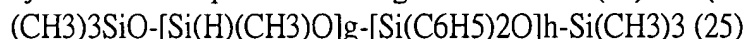
[Formula 3]



(As for R21 and R22, the alkyl group of carbon numbers 1-6 or a phenyl group, and R23 show the alkyl group or aralkyl radical of carbon numbers 1-10 among a formula.)  $0 \leq d \leq 8$  and e express  $2 \leq e \leq 10$ , and f expresses the integer of  $0 \leq f \leq 8$ , and d fills  $3 \leq d+e+f \leq 10$ . etc. -- a compound can be used.

[0072] Even if it uses these independently and they mix and use two or more sorts, they are not cared about.

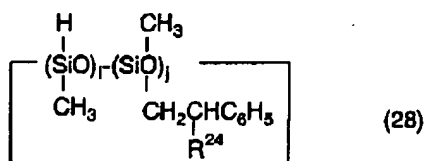
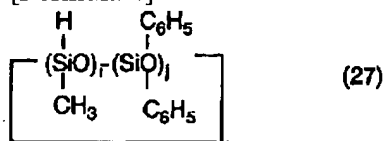
The chain-like siloxane expressed with the following general formula (25) which has a phenyl group from a viewpoint of compatibility with an acrylic polymer (meta), and (26) also in these siloxanes, and the cyclosiloxane expressed with a general formula (27) and (28) are desirable.



(R24 shows hydrogen or a methyl group among a formula.) g shows  $2 \leq g \leq 100$ , and h shows the integer of  $0 \leq h \leq 100$ . C<sub>6</sub>H<sub>5</sub> show a phenyl group.

[0073]

[Formula 4]



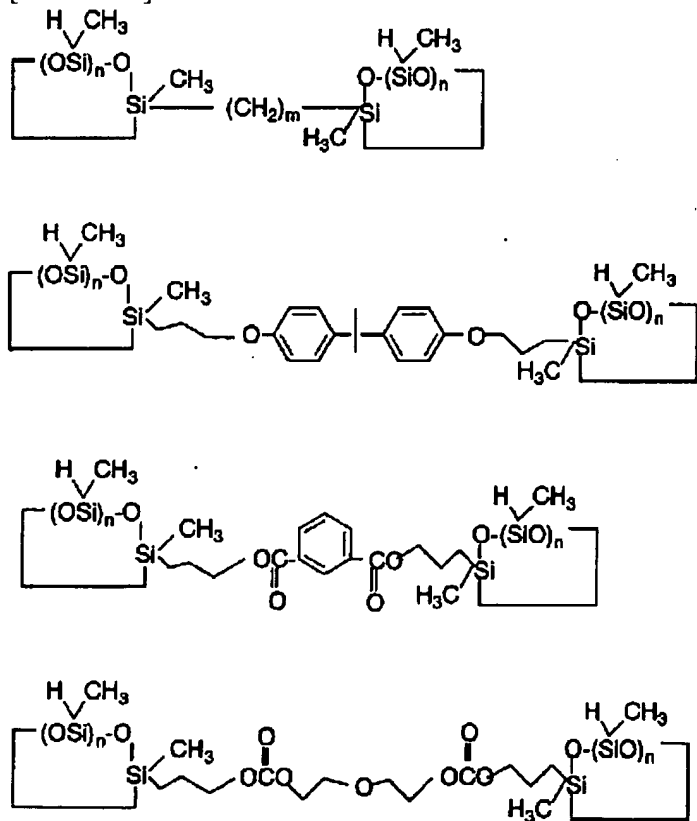
(R24 shows hydrogen or a methyl group among a formula.) The integer with which  $i$  fills  $2 \leq i \leq 10$ , and  $j$  fills  $0 \leq j \leq 8$  and  $3 \leq i+j \leq 10$  is shown. C6H5 show a phenyl group.

(B) As a compound which has at least one hydrosilyl radical of a component, the compound which is made to carry out the addition reaction of the hydrosilyl radical content compound expressed to (28) also after a reaction as some hydrosilyl radicals remain, and is obtained from a general formula (22) to the low molecular weight compound which has two or more alkenyl radicals in a molecule can also be used further. As a compound which has two or more alkenyl radicals, various kinds of things can be used into a molecule. If it illustrates, carbonate system compounds, such as ester system compounds, such as ether system compounds, such as - diaryl bisphenol A, and hydrocarbon system compound [, such as 1, 4-pentadiene, 1, 5-hexadiene 1, 6-heptadiene 1, 7-OKUTA diene, 1, 8-nonadiene 1, and 9-deca diene, ], O, and O'3, 3'-diaryl bisphenol A, diallyl phthalate, diallyl isophthalate, triallyl trimellitate, and tetra-allyl compound pyromellitate, and diethylene-glycol diaryl carbonate, will be mentioned.

[0074] This compound can be obtained by dropping slowly the alkenyl radical content compound mentioned from the above-mentioned general formula (22) to the bottom of existence of a hydrosilylation catalyst, and a top to the hydrosilyl radical content compound of the excessive amount shown in (28). In consideration of the compatibility to the polymer of the (A) component, the following are still more desirable among such compounds in the acquisition ease of a raw material, and the ease of carrying out of removal of the siloxane used superfluously.

[0075]

[Formula 5]



( $n$ は2 ~4 の整数,  $m$ は5 ~10 の整数)

Although the [creation approach of hardened material] polymer (A) and a curing agent (B) are mixable at a

rate of arbitration, it is desirable that the mole ratio of an alkenyl radical and a hydrosilyl radical is in the range of 5-0.2 from the field of hardenability, and it is still more desirable that it is especially 2.5-0.4. If smaller [ if a mole ratio becomes five or more, only a hardened material with inadequate hardening and small reinforcement with stickiness will be obtained, and ] than 0.2, since a hydrosilyl radical [ activity / in a hardened material / after / hardening ] remains in large quantities, a crack and a void occur, it will be uniform and a hardened material with reinforcement will not be obtained.

[0076] Although the hardening reaction of a polymer (A) and a curing agent (B) advances by mixing and heating two components, in order to advance a reaction more quickly, it can add a hydrosilylation catalyst. It is not limited especially as such a hydrosilylation catalyst, for example, radical initiators, such as organic peroxide and an azo compound, and a transition metal catalyst are mentioned.

[0077] It is not limited especially as a radical initiator. For example, G t-butyl peroxide, 2, the 5-dimethyl -2, 5-JI (t-butylperoxy) hexane, 2, the 5-dimethyl -2, 5-JI (t-butylperoxy)-3-hexyne, Dialkyl peroxide like dicumyl peroxide, t-butyl cumyl peroxide, alpha, and alpha'-bis(t-butylperoxy) isopropylbenzene, Benzoyl peroxide, p-chloro benzoyl peroxide, m-chloro benzoyl peroxide, 2, 4-dichlorobenzoyl peroxide, diacyl peroxide like lauroyl peroxide, Peroxy-acid ester like perbenzoic-acid-t-butyl, fault JI carbonic acid diisopropyl, Peroxi dicarbonate [ like fault JI carbonic acid G 2-ethylhexyl ], 1, and 1-JI (t-butylperoxy) cyclohexane, 1, and 1-JI (t-butylperoxy) - Peroxy ketal like a 3, 3, and 5-trimethyl cyclohexane etc. can be mentioned.

[0078] Moreover, a complex with the thing which it is not limited [ thing ] especially as a transition metal catalyst, for example, made support, such as a platinum simple substance, an alumina, a silica, and carbon black, distribute a platinum solid-state, chloroplatinic acid, chloroplatinic acid, alcohol, an aldehyde, a ketone, etc., a platinum-olefin complex, and a platinum (0)-divinyl tetramethyl disiloxane complex are mentioned. As an example of catalysts other than a platinum compound, RhCl (PPh<sub>3</sub>)<sub>3</sub>, RhCl<sub>3</sub>, RuCl<sub>3</sub>, IrCl<sub>3</sub>, FeCl<sub>3</sub>, AlCl<sub>3</sub>, PdCl<sub>2</sub> and H<sub>2</sub>O, NiCl<sub>2</sub>, and TiCl<sub>4</sub> grade are mentioned. These catalysts may be used independently, and it does not matter even if it uses two or more kinds together. Although there is especially no limit as an amount of catalysts, it is good for using in the range of 10<sup>-1</sup> to ten to 8 mol to use in the range of 10<sup>-3</sup> to ten to 6 mol often and preferably to one mol of alkenyl radicals of the (A) component. If fewer than ten to 8 mol, hardening will not fully advance. Moreover, since the hydrosilylation catalyst is expensive, it is desirable not to use ten - one or more mols.

[0079] In order to adjust physical properties, various kinds of additives, for example, aging prevention material, a filler, a plasticizer, a physical-properties regulator, a storage stability amelioration agent, etc. may be blended with the hardenability constituent for shaping of this invention.

[0080] Although an antioxidant is not necessarily required since a vinyl system polymer is originally a polymer excellent in endurance, a well-known antioxidant and an ultraviolet ray absorbent can be used suitably conventionally.

[0081] Especially as a filler which can be blended, it is not limited, for example, an impalpable powder silica, a calcium carbonate, clay, talc, titanium oxide, a zinc white, diatomaceous earth, a barium sulfate, carbon black, etc. are mentioned. The balance of viscosity and physical properties to an impalpable powder silica is desirable especially. Since side reaction has \*\*\*\* possibility in hardening reaction time when many moisture is contained, an anhydrous silica is still more desirable. It is desirable especially in order that what carried out non-dense water treatment of the front face of an anhydrous silica may tend to discover the fluidity suitable for shaping.

[0082] As a plasticizer, for the purpose, such as adjustment of physical properties, and accommodation of description, dibutyl phthalate, Phthalic ester, such as diheptylphthalate, di(2-ethylhexyl) phthalate, and butyl benzyl phthalate; Dioctyl adipate, Non-aromatic dibasic acid esters, such as dioctyl sebacate; Diethylene glycol dibenzoate, The ester of polyalkylene glycols, such as TORIECHIRENGURIKORUJIBENZOETO; Tricresyl phosphate, phosphoric ester [ , such as tributyl phosphate, ]; -- chloroparaffin; -- about hydrocarbon

system oils, such as alkyl diphenyl and partial hydrogenation terphenyl, etc., although two or more sorts can use it, mixing, they are not necessarily independence or the thing to need. In addition, these plasticizers can also be blended at the time of polymer manufacture.

[0083] The storage stability amelioration agent which can be blended will not be limited especially if a remarkable change of the cure rate after thickening at the time of storage of this constituent and storage can be suppressed, for example, benzothiazole, dimethylmalate, etc. are mentioned.

[0084] Although there is especially no limit about hardening conditions, generally it is preferably good to make [ 0 degree C - 200 degrees C / 30 degrees C - 150 degrees C ] it harden at 80 degrees C - 150 degrees C still more preferably. Thereby, the hardenability for shaping can be acquired in a short time.

[0085] Especially as the shaping approach of the hardenability constituent for shaping of this invention, it is not limited but various kinds of shaping approaches currently generally used can be used. For example, cast molding, compression molding, tolan FUFA shaping, injection molding, extrusion molding, rotational casting, blow molding, thermoforming, etc. are mentioned. Especially automation and continuation-izing are possible and what is depended on injection molding from a viewpoint of excelling in productivity is desirable.

[0086] The Plastic solid acquired from the hardenability constituent for shaping of this invention can be widely used centering on a gasket and packing as a Plastic solid in which rubber elasticity is shown. For example, in the automobile field, it can be used for the sealant for airtight maintenance, the vibration isolation material of glass, the vibroisolating material like Body Manufacturing Division especially a window seal gasket, and the gasket for door glass as a body part article. As chassis components, it can be used for the engine and suspension rubber, especially engine-mount rubber for vibrationproofing and sound isolation. As engine components, it can be used for the hose the object for cooling, the object for fuel supply, for exhaust air control, etc., the sealant for engine oils, etc. Moreover, it can be used also for exhaust gas purifying train components and brake components. In the household-electric-appliances field, it can be used for packing, an O ring, a belt, etc. Specifically The decoration for lighting fitting, waterproofing packing, rubber vibration insulators, and insect control packing Vibrationproofing and absorption of sound for cleaners, and an air sealant, dripproof covering for electric water heaters, Waterproofing packing, heater section packing, polar-zone packing, a relief valve diaphragm, The hose for gas-fires sake warmers, waterproofing packing, a solenoid valve, a steam microwave oven, and waterproofing packing for jar rice cookers, Feed water tank packing, a water absorption bulb, water receptacle packing, a connection hose, a belt, Oil packing for burning appliances, such as incubation heater section packing and a steamy diffuser seal, An O ring, drain packing, a pressurization tube, a ventilation tube, \*\* and inhalation-of-air packing, Loudspeaker gaskets for audio equipments, such as a rubber vibration insulator, oil-supply-port packing, oil gage packing, a feed tube, a diaphragm valve, and an airpipe, a loudspeaker edge, a turntable sheet, a belt, a pulley, etc. are mentioned. In the construction field, it can be used for a structural steel worker gasket (zipper gasket), pneumatic structure roofing, a water blocking material, a fixed form sealing material, a vibroisolating material, a sound insulating material, a setting block, sliding material, etc. In the sport field, it can be used for all-weather mold pavement material, a gymnasium floor, etc. as a sport floor, and sole material, insole material, etc. can be used for a golf ball etc. as a ball for ball games as sports shoes. In the rubber vibration insulator field, it can be used for the rubber vibration insulator for automobiles, the rubber vibration insulator for rail cars, the rubber vibration insulator for aircrafts, a fender, etc. In the ocean and the engineering-works field, as a structural material, a rubber expansion joint, bearing, a water stop, A tarpaulin, the rubber dam, elastic pavement, vibrationproofing putt, a protection object, etc. as a construction submaterial Rubber shuttering, A rubber packer, a rubber skirt board, a sponge mat, a mortar hose, a mortar strainer, etc., A rubber buoy, suppression-of-waves material, etc. can be used for an oil fence, a silt fence, antifouling material, a marine hose, a dredging hose, an oil skimmer, etc. as environmental preservation goods as safety-practice goods, such as rubber sheets and an air hose, as a construction auxiliary material. In addition, it can be used for plate rubber, a mat, a form plate, etc.

[0087]

[Example] Although the concrete example of this invention is combined with the example of a comparison and explained below, this invention is not limited to the following example.

[0088] The "weight section" and "% of the weight" are expressed the "section" and "%" among the following example and the example of a comparison, respectively.

[0089] "Number average molecular weight" and "molecular weight distribution (ratio of weight average molecular weight and number average molecular weight)" were computed among the following example by the standard polystyrene converting method for having used gel permeation chromatography (GPC). However, chloroform was used as what was filled up with polystyrene bridge formation gel as a GPC column (shodex GPC K-804; Showa Denko K.K. make), and a GPC solvent.

(Example 1 of manufacture) CuBr (36.02g, 0.2511 mols) was taught to the separable flask of 10L with reflux tubing and an agitator, and the nitrogen purge of the inside of a reaction container was carried out to it. The acetonitrile (618mL) was added and it stirred for 15 minutes at 70 degrees C among the oil bath. Butyl acrylate (360mL, 2.51 mols), an ethyl acrylate (500mL, 4.62 mols), acrylic-acid 2-methoxy ethyl (375mL, 2.91 mols), 2, 5-dibromo adipic-acid diethyl (150.68g, 0.419 mols), and pentamethyl diethylenetriamine (2.18mL, 1.81g, 10.46mmol) (it expresses triamine after this) were added to this, and the reaction was started. Butyl acrylate (1440mL), an ethyl acrylate (2002mL), and acrylic-acid 2-methoxy ethyl (1498mL) were continuously dropped over 210 minutes, carrying out heating stirring at 70 degrees C. Triamine (7.63mL, 6.33g, 36.5mmol) was added in the middle of dropping of a monomer. From reaction initiation, 1, 7-OKUTA diene (1236mL, 922g, 8.37 mols), and triamine (26.16mL, 21.71g, 0.125 mols) were added after 330-minute progress, and heating stirring was succeedingly carried out at 70 degrees C for 250 minutes.

[0090] After diluting the reaction mixture with toluene and letting an activity alumina column pass, the alkenyl radical end copolymer {copolymer:copolymer [1] of alkenyl end Pori (butyl acrylate, an ethyl acrylate, acrylic-acid methoxy ethyl)} was obtained by carrying out reduced pressure distilling off of the volatile matter. The number average molecular weight of a copolymer [1] was 19600, and molecular weight distribution were 1.24.

[0091] Copolymer [1] (1.90kg), potassium acetate (98.2g), N, and N-dimethyl acetic amide (1.9L) was taught to 5with reflux tubing L separable flask, and heating stirring was carried out at 70 degrees C under the nitrogen air current for 9 hours. It diluted with toluene, after removing N and N-dimethyl acetic amide by the scale loss draft. A part for an insoluble solid-state (KBr and surplus benzoic-acid potassium) was filtered by the activity alumina column in toluene. The copolymer [2] was obtained by carrying out reduced pressure distilling off of the volatile matter of a filtrate.

[0092] A copolymer [2] (0.8kg), silicic acid aluminum (177g, the product made from consonance chemistry, KYO WORD 700PEL), and toluene (3.2L) were taught to 5with reflux tubing L separable flask, and heating stirring was carried out at 100 degrees C under the nitrogen air current for 3 hours. After filtration removed silicic acid aluminum, the vinyl group end copolymer (copolymer [3]) was obtained by carrying out reduced pressure distilling off of the toluene of a filtrate. By GPC measurement (polystyrene conversion), the number average molecular weight of the obtained copolymer was 20300, and molecular weight distribution were 1.31. It is 1H about the number of the vinyl groups of the average introduced into per copolymer 1 molecule. When asked by NMR analysis, they were about 2.7 pieces.

(Example 1) 1, 1 and 3 of copolymer [3]100g obtained in the example 1 of manufacture, chain-like siloxane 6.9g which contains an average of five hydrosilyl radicals and an average of five alpha-methyl-styrene radicals in a molecule, and zerovalent platinum, 3-tetramethyl - Degassing of the 2.14ml of the 1 and 3-divinyl disiloxane complexes was \*\*\*\*\*ed and carried out at the room temperature. This mixture showed fluidity sufficient at a room temperature. When slushing this mixture into shuttering and carrying out hardening care of health at 150 degrees C, hardened materials enough in 10 minutes were obtained. In addition, the amount of the chain-like siloxane used made 1.8Eq and the amount of the platinum catalyst used  $1.5 \times 10^{-4}$ Eq by the mole ratio by the mole ratio of a hydrosilyl radical to the vinyl group of a copolymer.

(Example 2) 1, 1 and 3 of copolymer [3]100g obtained in the example 1 of manufacture, Aerosil (R-974: product made from Japanese Aerosil) 20g, chain-like siloxane 6.9g which contains an average of five hydrosilyl radicals and an average of five alpha-methyl-styrene radicals in a molecule, and zerovalent platinum, 3-tetramethyl - Degassing of the 2.34ml of the 1 and 3-divinyl disiloxane complexes was \*\*\*\*\* (ed) and carried out at the room temperature. This mixture showed fluidity sufficient at a room temperature. After putting this mixture in a cartridge, it extruded from the cartridge to the shuttering of a fixed configuration. Self-leveling was carried out when put at 50 degrees C for 10 minutes. Hardened materials enough in 10 minutes were obtained maintaining a configuration as it is, when carrying out hardening care of health of this at 150 degrees C. In addition, the amount of the chain-like siloxane used made 1.8Eq and the amount of the platinum catalyst used  $2 \times 10^{-4}$ Eq by the mole ratio by the mole ratio of a hydrosilyl radical to the vinyl group of a copolymer.

(Example 1 of a comparison) 1, 1 and 3 of polyoxypropylene glycol 100g of the molecular weight 10,000 [ about ] by which the end was alkenyl-ized, chain-like siloxane 6.9g which contains an average of five hydrosilyl radicals and an average of five alpha-methyl-styrene radicals in a molecule, and zerovalent platinum, 3-tetramethyl - Degassing of the 0.64ml of the 1 and 3-divinyl disiloxane complexes was kneaded and carried out at the room temperature. When carrying out hardening care of health at 150 degrees C, hardened materials enough in 10 minutes were obtained. In addition, the amount of the chain-like siloxane used made 1.5Eq and the amount of the platinum catalyst used  $5.0 \times 10^{-5}$ Eq by the mole ratio by the mole ratio of a hydrosilyl radical to the vinyl group of a polymer.

[0093] The degree of hardness (JIS A) of the hardened material produced in the example 1 - the example 2, and the example 1 of a comparison and the oilproof (JIS K 6820) result were shown in Table 1.

[0094]

[Table 1]

	硬度	耐油性(重量増分:%)	
		室温×70h	150℃×70h
実施例1のアクリル末端ポリ(アクリル酸ブチル、エチル、メタクリル)共重合体単独硬化物	15	0.3	2
実施例2のアクリル末端ポリ(アクリル酸ブチル、エチル、メタクリル)共重合体配合硬化物	26	0.3	2
比較例1のアクリル末端ポリブテンレシコール単独硬化物	24	19	130

The machine physical properties after hardening care of health of the hardened material produced in the example 1 - the example 2, and the example 1 of a comparison were shown in Table 2.

[0095]

[Table 2]

	M <sub>50</sub> (MPa)	M <sub>100</sub> (MPa)	T <sub>max</sub> (MPa)	E <sub>b</sub> (%)
実施例1のアクリル末端ポリ(アクリル酸ブチル、エチル、メタクリル)共重合体単独硬化物	0.13	0.23	0.54	220
実施例2のアクリル末端ポリ(アクリル酸ブチル、エチル、メタクリル)共重合体配合硬化物	0.23	0.51	3.61	380
比較例1のアクリル末端ポリブテンレシコール単独硬化物	0.37	0.56	0.57	100

The compression set property after hardening care of health of the hardened material produced in the example 1 - the example 2, and the example 1 of a comparison (JIS K 6262, however a test condition were made into 150 degrees C and 72 hours.) was shown in Table 3.

[0096]

[Table 3]

	圧縮永久歪み (%)
実施例 1 のアクリル末端ポリ(アクリル酸ブチル、 エチル、メキシエチル)共重合体単独硬化物	15
実施例 2 のアクリル末端ポリ(アクリル酸ブチル、 エチル、メキシエチル)共重合体配合硬化物	40
比較例 1 のアクリル末端 ポリブテン-1単独硬化物	— (原形 留めず)

[0097]

[Effect of the Invention] Since the hardenability constituent for shaping of this invention is excellent in workability and excellent in hardenability by the ability kneading compounding agents, such as a filler, in the liquefied condition, it can be fabricated in a short time. Moreover, the Plastic solid which makes it come to harden this has sufficient mechanical characteristic, thermal resistance, and oilproof.

[Translation done.]